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14. Abstract:

The conventional means of searching for new materials, in this case efficient thermoelectrics, is to synthesize a large number of compounds and investigate each in detail as a function of materials parameters, such as preparation conditions and doping levels. Each compound thus represents one point in a phase space determined by electronic and structural parameters. With the use of pressure one can continuously adjust the interaction parameters and follow the change in properties for each compound. During the period of this grant, we demonstrated that antimony bismuth telluride can be pressure tuned to exhibit a thermoelectric figure of merit that is at least a factor of two higher than any known material at ambient pressure. This demonstration that higher ZT is possible under pressure is a valuable "existence proof". We have developed an understanding of origin of the increase in the thermoelectric power associated with an electronic topological transition. This new understanding suggests future research directions for ambient pressure chemical tuning.

Final Report

ONR AWARD Number: N00014-97-1-0565

Project Title: Pressure Tuning of Intermediate Valence and Multiband Semiconductor Thermoelectric Materials

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Pressure Tuning of Intermediate Valence and Multiband Semiconductor Thermoelectric Materials: Final Report

This award was for work performed from April 1997 to April 2001 under grant number N00014-97-0565. The award funded research aimed at finding thermoelectric materials with higher figures of merit than currently known materials by means of a pressure tuning approach. The conventional means of searching for new materials, in this case efficient thermoelectrics, is to synthesize a large number of compounds and investigate each in detail as a function of materials parameters, such as preparation conditions and doping levels. Each compound thus represents one point in a phase space determined by electronic and structural parameters. With the use of pressure one can continuously adjust the interaction parameters and follow the change in properties for each compound. Thus a much larger volume of this interaction phase space can be "scanned" in a short time without the large effort necessary to produce the thousands of materials necessary to do so with the conventional approach. During the period of this grant, we demonstrated that antimony bismuth telluride can be pressure tuned to exhibit a thermoelectric figure of merit that is at least a factor of two higher than any known material at ambient pressure. This demonstration that higher ZT is possible under pressure is a valuable "existence proof". Our current research goals are now focused on chemical modification of the semiconductors that have been successfully pressure tuned with the goal of obtaining improved thermoelectric properties at atmospheric pressure. We have developed an understanding of origin of the increase in the thermoelectric power associated with an electronic topological transition. This new understanding suggests future research directions for ambient pressure chemical tuning. An NSF focused research proposal involving the three PI's on this ONR grant has recently been recommended for funding.

Our first technical challenge was to develop methods for measuring thermoelectric power under pressure. We developed a diamond anvil cell technique for measuring the thermoelectric power and electrical conductivity under pressure. Careful measurements of several standards were performed to confirm the accuracy of this technique. Mahan assisted with theoretical investigations of the accuracy of the experimental apparatus that was used. Next, candidate thermoelectric materials from several laboratories across the country, including those of Badding, DiSalvo, Kanatzidis, JPL, and Marlo Industries, were pressure tuned while measuring the thermoelectric power. A rich variety of behaviors were observed. The thermoelectric power of several materials, including antimony bismuth telluride (figure 1), was observed to increase by as much as a factor of two or three. To determine ZT at high pressure, it is also necessary to have the electrical conductivity and the thermal conductivity. We found that the electrical conductivity of $Sb_{1.5}Bi_{0.5}Te_3$ increases by a factor of 2.74 from 967 S/cm at 0.1 MPa to 2650 S/cm upon compression to 1.7 GPa in a diamond anvil cell. It is possible to measure thermal conductivity at high pressure, but it is challenging and relatively few measurements have been made. Instead, we placed an upper bound on the increase in the thermal conductivity under pressure (see references). Using the maximum value of the thermoelectric power at 1.7 GPa, 305 μV/K, and our measured value for the electrical conductivity and upper bound on the thermal conductivity, ZT is 2.2. This is significantly larger than any reported ZT at ambient pressure.

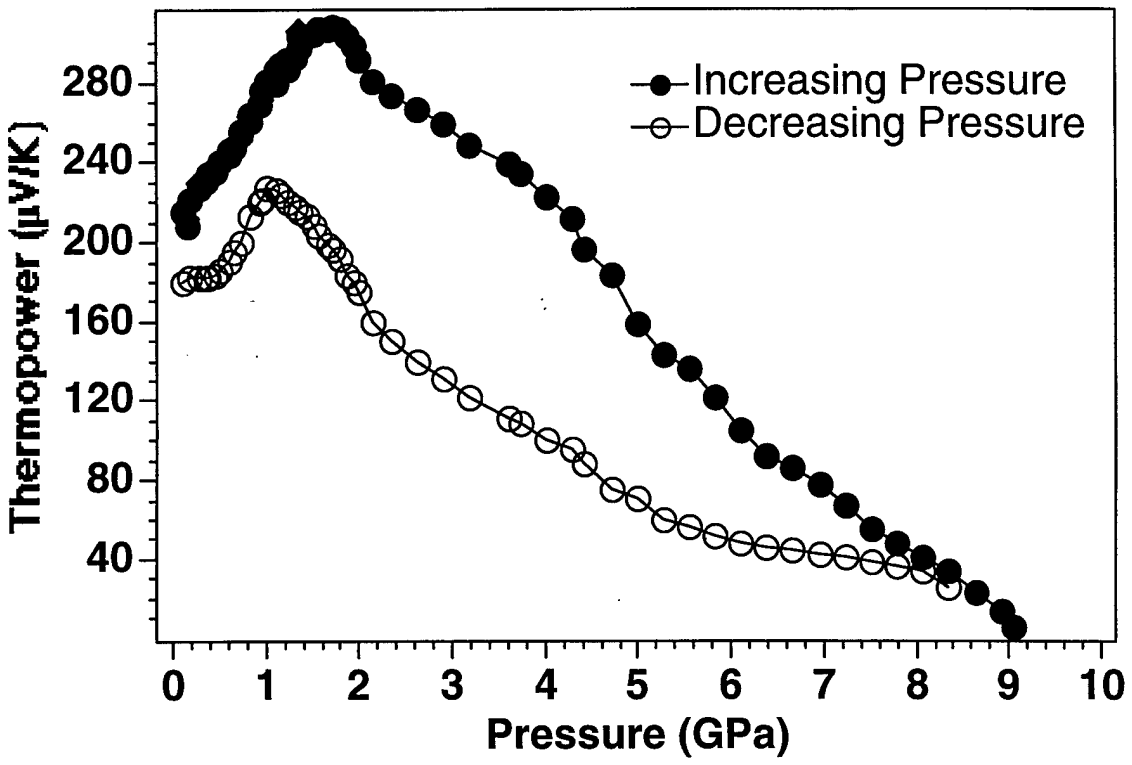

Figure 1. Thermoelectric power versus pressure for $Sb_{1.5}Bi_{0.5}Te_3$. The pressure was initially increased to 1.5 GPa, then released. Upon release of pressure the thermoelectric power returned to the same ambient pressure value. The data points from this first run in the increasing and decreasing pressure directions are coincident with the low pressure data in the increasing pressure direction from the second run, in which the sample was compressed to 9 GPa. Therefore, the data points from the first run are not indicated separately in the legend.

Sharp maxima in the thermoelectric power that resemble the behavior observed for $Sb_{1.5}Bi_{0.5}Te_3$ have been observed in metallic elements, intermetallic compounds, and heavily doped semiconductors that undergo an electronic topological transition (ETT). An ETT occurs when a band extremum, which is associated with a Van Hove singularity in the density of states, crosses the Fermi energy resulting in a change in the topology of the Fermi surface and a strong energy dependence to the electronic density of states near the Fermi energy. There is a sharp maximum in the thermoelectric power of doped Bi_2Te_3 upon hydrostatic compression at liquid helium temperature as a result of an ETT suggesting that it is plausible for an ETT to occur in the isoelectronic doped alloy $Sb_{1.5}Bi_{0.5}Te_3$.

The results obtained during the period of this grant demonstrate that in principle improved ZT values are possible. It would be desirable to now reproduce the improved thermoelectric behavior observed at high pressure at ambient pressure. Electronic

topological transitions can be induced not only by pressure but also by means of alloying. Metallic lithium-magnesium alloys, for example, can exhibit a peak in the thermoelectric power at temperatures below 78K that is associated with an electronic topological transition. This peak broadens and becomes less pronounced at higher temperatures. However, peaks in thermoelectric power associated with an ETT have been observed in compressed metals at ambient temperature, indicating that it may be possible for similar behavior to occur in alloys. Such compounds might exhibit improved thermoelectric properties. We are now investigating whether an ETT can be induced in Sb_2Te_3 or Bi_2Te_3 by means of alloying and this approach could also be applied to many other semiconductor materials.

On the theoretical side, the initial efforts were concentrated on understanding in detail the thermoelectric properties of intermediate valence rare-earth compounds. Simple estimates show that a dimensionless figure of merit of ZT~ 1 can be attained if the Seebeck coefficient is larger than 160 μV/K. The question is whether this is possible, or whether there is any fundamental limitation on ZT for these systems. Mahan has shown that the single site Anderson model can produce values of the Seebeck coefficient large enough to explain the experimentally observed values of 80 to 125 μV/K in $CePd_3$ (see figure). The results depend on both the amount of hybridization, Δ, and the temperature, T. Later efforts included theoretical investigation of electronic topological transitions in antimony bismuth telluride and:

(i) Rare earth thermoelectrics: a large computer code was written to describe the Seebeck coefficient in metallic alloys which contain local magnetic moments such as those provide by transition metal and rare earth ions. This computer code was run for many different parameter sets, which include all rare-earth configurations. In metals, good thermoelectric properties depend primarily on having a large value of the Seebeck coefficient.
(ii) Electronic structure calculations: The computer code WIEN97 was run to determine the atomic arrangements and energy band structure of crystals relevant to the group research. After DiSalvo showed that the highest Seebeck coefficient was in CePd3, the energy bands were calculated for this material. When Badding found that the thermoelectric properties of bismuth telluride and antimony telluride increased under pressure, the energy bands were calculated for these materials under pressure.
(iii) Modeling the pressure experiments: Mahan has worked with Badding to develop a computer model of the pressure experiment. The important variables are how the local heating by the laser causes heat which spreads throughout the experimental apparatus. When the voltages are measured at the various contacts, do they truly represent only the Seebeck of the sample, or are there other factors?
(iv) Currents through interfaces: Bartkowiak and Mahan have derived the theory of how heat and electricity flows through interfaces, and multilayer systems. They used the Boltzmann equation to derive macroscopic equations, which are then solved on the computer for multilayer systems.

Further technical details can be found in the publication list at the end of this report.

This research was performed by undergraduate, graduate, and post doctoral students as part of their professional training. Here is a list of individuals supported by funds from this award and their current status:

Penn State University:

Graduate Students:
Deborah Polvani, PhD. 2000 - employed full time at General Electric Corporation

Post-doctoral Associates:
Masashi Hasegawa - research Associate at the Institute of Solid State Physics, Tokyo, Japan
JinFang Meng - currently studying at University of Ottowa
Chandrashekar Nagar - employed at Indira Gandhi Center for Atomic Research, India

Cornell University:

Undergraduates:
Kimberly Regan – currently a graduate student in Chemistry at Princeton University
Josh Balcs: - finishing junior year at Cornell

Graduate Students:
Kevin Proctor – PhD. 2000, employed full time at Intel Corporation
Ying Wang – PhD. 2000, employed full time at KLA-Tencor
Christopher Jones – PhD. 1999, employed full time at Bell Labs, Lucent Technologies
Kristing Poduska, PhD. 2001, postdoctoral position at York University, Toronto, Canada
Christopher Hoffman - currently finishing fourth year in graduate school
Thomas Reynolds – currently finishing second year in graduate school

Postdoctoral Associates:
Thomas Braun - employed full time at Cornell Information Technologies

University of Tennessee:

Post-doctoral Associates:
Miroslaw Bartkowiak – employed full time at Cygnus corporation

Technical Publications resulting from work supported by this award:

(1) Polvani, D. A.; Meng, J. F.; Shekar, N. V. C.; Sharp, J.; Badding, J. V. "Large improvement in thermoelectric properties in pressure- tuned p-type $Sb_{1.5}Bi_{0.5}Te_3$", *Chem. Mat.* **2001**, *13*, 2068.

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